Positron investigations of thin film silicon for photovoltaics

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ABSTRACT

Positron defect profiling and beam based positron lifetime studies have been performed on thin film silicon samples manufactured by a variety of techniques. The goal is to shed unique information on the type of defects and their influence on the properties of the materials pertinent to photovoltaic applications. It was discovered that amorphous silicon films exhibit a more complex response to light soaking that previously observed. In addition to the Staebler Wronski effect it appears that an irreversible change occurs upon light soaking. The Staebler Wronski effect, reversible by annealing, was not observed and may be associated with a intermediate defect, which has stronger trapping character to positrons than the defect responsible for the Staebler Wronski effect. Samples of crystalline silicon thin films were examined for comparison and beam based positron lifetime measurements were carried out to investigate the nature of the defects involved. Light soaking and low temperature data will also be presented.

1. Introduction

All models of the Staebler-Wronski effect [1-4] invoke the breakup of Si-H bonds and the conversion of bound H to mobile H by the incident light. High hydrogen dilution ratios promote the growth of microcrystalline silicon [5]. It was observed that intense illumination cause additional degradations in efficiency, which is not reversible [6]. Both effects obviously change the electrical properties of the material, making an investigation with positron annihilation spectroscopy (PAS) interesting and is sensitive to vacancy defects to 1 part and 10^{-7} atomic concentration. The current status of our findings will be presented and discussed below following a brief introduction into the capabilities of PAS. The positron annihilation spectroscopy will be introduced by using a-Si samples grown under different hydrogen dilution ratios.

Positrons will annihilate with electrons predominantly via the emission of two photons. Energy and momentum conservation causes small angular deviations from antiparallel emission and Doppler shifts from the mean photon energy of 511 keV. The positron wave function tends to concentrate where the positive atom cores are spaced farther than on average in the sample and localized in open volume equivalent of vacancies or larger. The positron at the time of annihilation is in thermal equilibrium with the surrounding lattice. Thus, the measured Doppler shifts, and the broadening of the annihilation line when many events are detected are due only to the momentum distribution of the electrons at the site of annihilation. With increasing open volume the average momentum (or increasing positron lifetime) of an annihilation rate and consequently the measured Doppler shifts. The annihilation photon line shape narrows and the mean positron lifetime increases. At the same time the electron density decreases with open volume size. The reduced overlap of electron and positron wave function lowers the annihilation rate (increases the lifetime) of the positron. Changes in thin film silicon due to illumination can thus be observed with positron Doppler and lifetime measurements. The charge state of the sites determines whether positrons are attracted to them (positively charged) or sensitive (neutral or negatively charged).

Samples grown by PECVD without H dilution and with H dilution were grown at ~200C to a thickness of 0.25 μm (*i*-layer) on a stainless steel substrate and light-soaked for 0, 120, 300, and 625 hrs in 1 sun with a various H-dilution ratios and no dilution were studied. Some samples were annealed subsequent to light soaking. Positron lifetime data will also be presented.

2. Experimental

Figure 1 shows the measure of "open volume" versus mean positron implantation depth for a H-diluted and a non-diluted sample. H-dilution reduces the value from one equivalent of vacancies. Beyond 160 nm mean depth an increasing fraction of positrons annihilates from the substrate. The change and curvature in the data from the surface to the a-Si layer is used to extract annihilation site concentrations relative to a "perfect" amorphous network or micro-crystalline regions. When the dilution ratio is increased to 3 and higher, this fraction drops by a factor of more than 20.

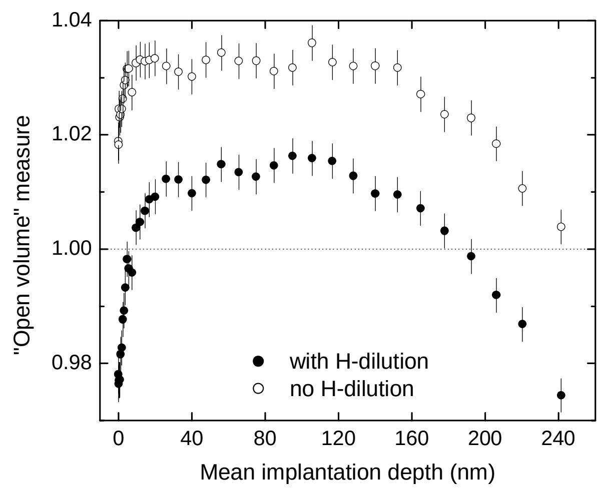

Figure 1: Open volume measure in as made a-Si samples produced with and without H-dilution versus mean positron implantation depth.

The effect due to light soaking is shown in figure 2. Short soaking periods of 300 hours and less show little effect; long soaking times of 600 hours increase the open defect concentration. At the same time the fraction of open volume sites steadily decreases in the non-diluted case and remains near constant in the H-diluted case.

To date only a small reversal of the light-soaking effect was observed following anneals of the samples at about 200 C for different periods of time.

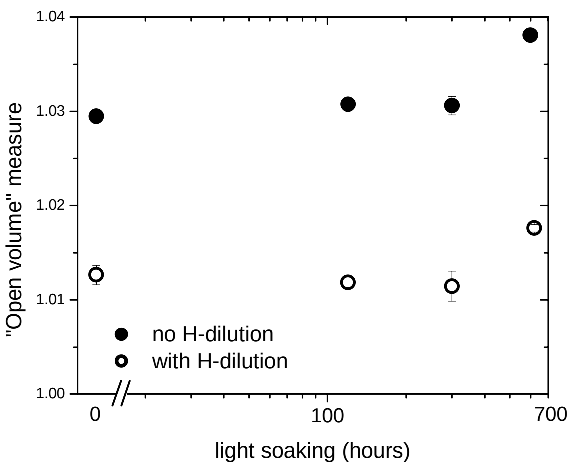

Figure 2: Change in open volume measure relative to single crystal silicon for different light soaking times.

Positron lifetimes have been measured on some of these samples. An increase in the lifetimes indicates an increase in the separation of the atomic sites. The evaluation of an average lifetime allows for the extraction of these trends. An increase in the mean lifetime is a consequence of an increase in either the size or the concentration of open volume sites (or a combination thereof). Figure 3 shows the results of preliminary data on amorphous silicon samples compared to a perfect single crystal silicon sample and silicon ribbon. The mean lifetime increases from single crystal silicon to H-diluted silicon to Si-ribbon and is largest in non-diluted amorphous Si. Light soaking under 1 standard sun for 620 hrs further increases the mean lifetime. Positron lifetimes have been measured recently by Britton et al on HW-CVD Si [7]. They report longer mean lifetimes of 330 ps, indicating that the samples studied here are far superior and are not associated with the intrinsic behavior of the films but with voids created during fabrication.

3. Results and Discussion

The positron data indicate that the a-Si samples studied here contain concentrations of open-volume type sites, most likely dangling bond and/or H-terminated dangling bond related. Their concentration decreases with increasing H-dilution ratios during formation. At the same time the fraction of micro-crystalline Si in the samples increases [8]. Light soaking in excess of 300 hours shows an increase in open volume, consistent with the interpretation that atomic H is removed. To date, however, the observed effect is not reversible by annealing, which is key to understanding this defect. Possibly, the reason can be found in the presence of a second defect in addition to the defect responsible for the Staebler-Wronski effect. The former traps positrons more efficiently than the shallower latter defect. The deeper lying defect could be below the Fermi level and thus not electrically active. However, this defect could be responsible for the permanent degradation observed after intense light exposure (7).

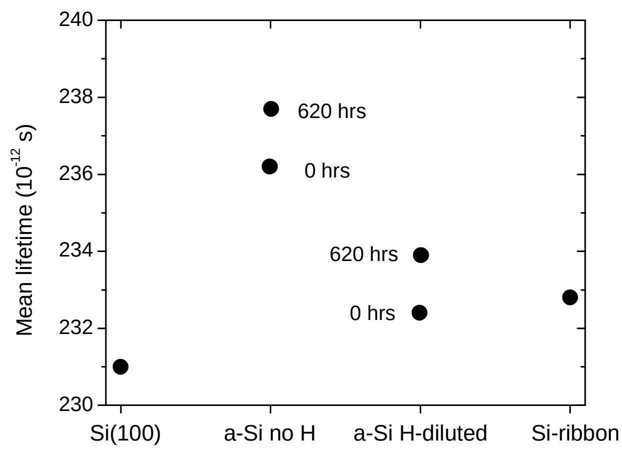

Figure 3: Mean lifetime of positrons in crystalline and amorphous silicon samples. The mean implantation depth was 50 nm.

To examine this possibility we initiated a new set of measurements on samples on glass substrates to be produced by Wronski. In addition to positron measurements these will be examined by time-resolved spectroscopy (requiring transparent substrates) by S. Dexheimer, WSU and with ESR measurements by C. Taylor, U of Uath.

Positron measurements will be extended to low temperatures to enhance the probability of trapping at both defects. Positron lifetime studies are under way to separate lifetimes from different trapping sites.

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